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[54] Name of invention: Fluidized-bed catalyst for propylene ammoxidation to produce acrylonitrile.

[57] Abstract:

This invention relates to a fluidized-bed catalyst for propylene ammoxidation to produce acrylonitrile, comprising silicon dioxide as support and a composite of the atomic ratio of the following formula:  $A_a B_b C_c Mg_d Mn_e W_f Fe_g Bi_h Mo_i O_x$ , wherein A is at least two elements selected from the group consisting of Li, Na, K, Rb, and Cs; B is at least one element selected from the group consisting of Co, Ni, Cr, Ca, Ce, La, Cu and V; C is at least one element selected from the group consisting of B, P and As. The catalyst of this invention is especially suited for use under conditions of slightly lower than normal reaction temperatures, low air to propylene ratios, higher reaction pressures and high loads. It maintains a high single pass yield rate of acrylonitrile, making it suitable for industrial use.

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## Claims

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1. A fluidized-bed catalyst for propylene ammoxidation to produce acrylonitrile, comprising silicon dioxide as support and a composite of the atomic ratio of the following formula:



where A is at least two elements selected from the group consisting of Li, Na, K, Rb and Cs;

B is at least one element selected from the group consisting of Co, Ni, Cr, Ca, Ce, La, Cu and V;

C is at least one element selected from the group B, P and As;

a = 0.01 to 1.5;

b = 0.1 to 10.0;

c = 0.0 to 0.6;

d = 0.8 to 7.5;

e = 0.01 to 2.5;

f = 0.05 to 1.5;

g = 0.1 to 4.0;

h = 0.2 to 2.5;

i = 12.0 to 14.5;

x = total number of oxygen atoms required to satisfy the valence requirement of the other elements present in the catalyst;

the content of silicon dioxide support in the catalyst is in the range of 30 to 70% by weight.

2. A catalyst based on claim 1, wherein a is in the range of 0.01 to 0.7.
3. A catalyst based on claim 1, wherein c is in the range of 0.01 to 0.45.
4. A catalyst based on claim 1, wherein d is in the range of 1.0 to 4.0.
5. A catalyst based on claim 1, wherein e is in the range of 0.2 to 1.5.
6. A catalyst based on claim 1, wherein f is in the range of 0.1 to 1.0

## Description

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### Fluidized-bed catalyst for propylene ammoxidation to produce acrylonitrile

The present invention relates to a fluidized-bed catalyst for propylene ammoxidation to produce acrylonitrile.

Acrylonitrile is an important organic industrial chemical produced by the reactivity of propylene ammoxidation. Continuous investigation has been made into obtaining a highly active and selective fluidized-bed catalyst for this purpose, resulting in a series of improvements in catalyst activity. Emphasis has been placed upon collocation of the active components in order to increase activity and selectivity of the catalyst, thereby increasing the single pass yield rate of acrylonitrile as well as the production load.

Thirty years of development in the industry now see processing capacity and market demand close to being in balance. In the quest to lower raw material consumption and increase processing capacities, the main trend in acrylonitrile production has evolved from an emphasis on building new production equipment and facilities to adapting existing production technologies. That, along with highly effective catalysts and the elimination of bottlenecks in production, can mean increases in acrylonitrile production capacities of 50 to 80%. The investment necessary is only 20 to 30% of that required for new equipment, which is a huge benefit from an economic standpoint.

Two problems will arise when modifying existing production facilities: 1) reaction pressure in fluidized-bed reactors will increase; 2) catalyst loads cannot be too large. Therefore, new catalysts should have higher propylene loads and should be able to withstand higher reaction pressures.

Reaction pressure in fluidized-bed reactors is determined by the drop in resistance of a series of heat exchangers, columns, and piping between the reactor outlet and the top of the absorption column. Due to a sizeable increase in outlet emissions brought about by an increase in processing capacity, resistance drops further. Also, if the thermal diffusion area isn't large enough, more heat exchange equipment will be needed, dropping resistance even further. Due to environmental demands, reaction emissions from absorption columns are not allowed to be discharged directly into the air, but instead must be sent to furnaces to be burned off. If an exhaust fan isn't used, pressure will have to be increased in the absorption column. Due to each of the factors cited above, at present the reactor's operating pressure will need to be increased by 0.5 to 1.0 times that of the original value, reaching more than 0.08 MPa.

The second problem cited above is the catalyst load (WWH). It is defined as the number of tons of propylene processed per ton of catalyst per hour. Due to increases in the amount of material fed into the reactor, if the catalyst load is invariant, the amount of catalyst loaded must correspondingly be increased. However, if the cooling water pipe in the fluidized-bed reactor isn't high enough, the catalyst might fluidize higher than the pipe. Also, the operating speed will be faster due to the increased feed of material into

the reactor. The combined effect of these two changes might be to affect a rise in the temperature of the dilute phase, leading to an increase in carbon dioxide and a decrease in the selectivity of the acrylonitrile. However, a higher WWH for the catalyst will prevent these problems.

In theory, increasing the WWH of the catalyst should mean increasing the catalyst's active capacity to adsorb propylene, but at present there are no reports of any element in a catalyst that is able to do as such.

Chinese patent CN 1021638C proposes a catalyst composed of the following:

$A_a B_b C_c Ni_d Co_e Na_f Fe_g Bi_h M_i Mo_j O_x$ ; wherein

A is potassium, rubidium, cesium, samarium and thallium; B is manganese, magnesium, strontium, calcium, barium, lanthanum and rare earth; C is phosphorus, arsenic, boron, antimony and chromium; M is tungsten and vanadium.

This catalyst can achieve higher single pass yields of acrylonitrile, but has a lower propylene load. Under higher reaction pressures there is a larger decrease in single pass yields. Further research has shown that there is a link between the effect of components B and M upon this catalyst's load and its performance under high pressure. Even though certain of the elements of component B function to increase single pass yields of acrylonitrile, they have a negative effect upon the increase in catalyst load and performance under high reaction pressures, and don't help the catalyst adjust to higher pressures and loads. Patent CN 1021638C stipulates that in the catalyst above the sum of i and j is 12, a constant. The present invention dispenses with this stipulation because when component M is increased, the molybdenum component decreases, affecting single pass yields of acrylonitrile.

US patents 5,093,299 and 5,212,137 introduce a catalyst composed of molybdenum, bismuth, iron, nickel, magnesium and cesium for an ammoxidation reaction to produce acrylonitrile. From the embodiments of these patents it can be seen that the catalyst does not include sodium. Even though the optional elements include rare earth metals cerium and chromium, they are still merely optional, and there is no example given where other rare earth elements are collocated with chromium and magnesium. The test conditions of the embodiments are a fixed-bed and a reaction temperature of 430°C, but no data is given for the actual reaction pressures or the operating loads of the tests. This fixed-bed does not, however, reflect the actual operating conditions of a fluidized-bed. The patents claim that the catalyst is able to function under slightly lower than normal reaction temperatures, and has higher catalytic activity and very good oxidation-reduction stability, and thus is suitable for use in conditions of lower air to propylene ratios.

Japanese patent JP 8-27089 introduces a method for manufacturing acrylonitrile using a catalyst composed of molybdenum, bismuth, iron, magnesium and tungsten for an ammoxidation reaction. The tests were conducted under conditions of normal pressure, but the patent does not give data for conditions of high pressure or high operating loads.

The goal of the present invention is to overcome the problems of higher reaction pressures and operating loads not dealt with for the catalyst in the patents mentioned above, offering a new fluidized-bed catalyst for producing acrylonitrile. This catalyst is suitable for use in conditions of slightly lower than normal reaction temperatures, higher reaction pressures and higher loads while maintaining high single pass yield rates of acrylonitrile.

The goal of the present invention will be realized with the following technology: a fluidized-bed catalyst for producing acrylonitrile comprising silicon dioxide as support and a composite of the atomic ratio of the following formula:



where A is at least two elements selected from the group consisting of Li, Na, K, Rb and Cs;

B is at least one element selected from the group consisting of Co, Ni, Cr, Ca, Ce, La, Cu and V;

C is at least one element selected from the group B, P and As;

$$a = 0.01 \text{ to } 1.5;$$

$$b = 0.1 \text{ to } 10.0;$$

$$c = 0.0 \text{ to } 0.6;$$

$$d = 0.8 \text{ to } 7.5;$$

$$e = 0.01 \text{ to } 2.5;$$

$$f = 0.05 \text{ to } 1.5;$$

$$g = 0.1 \text{ to } 4.0;$$

$$h = 0.2 \text{ to } 2.5;$$

$$i = 12.0 \text{ to } 14.5;$$

x = total number of oxygen atoms required to satisfy the valence requirement of the other elements present in the catalyst;

the content of silicon dioxide substrate in the catalyst is in the range of 30-70 percent by weight.

Within this proposal, the optimum range for a is 0.01 to 0.7, for c 0.01 to 0.45, for d 1.0 to 4.0, for e 0.2 to 1.5, and for f 0.1 to 1.0.

There are no special demands for the manufacture of the catalyst in this invention; it can be prepared according to conventional methods. First, mix the components of the catalyst into a solution, then mix the solution with the substrate to form a slurry. After spray drying into microspheres, calcinate to produce the catalyst. The preparation of the catalyst is best done according to the method in Chinese patent CN 1005248C.

The raw materials used to prepare the catalyst in this invention are as follows:

Molybdenum oxide or ammonium molybdate is used for the molybdenum component .

The phosphorus, arsenic and boron preferably originate from their corresponding acids or ammonium salts; tungsten originates from ammonium tungstate or tungsten oxide; chromium preferably originates from chromium trioxide, chromium nitrate, or their mixture; the remaining can originate from their nitrates, hydroxides or oxides, or salts which are decomposable to oxides.

The raw material for the substrate, silicon dioxide, can originate from silica sol, silica gel, or their mixture. If silica sol is used, its quality must meet the standard of Chinese patent CN 1005248C.

Once the slurry is formed it is heat-treated to solid content of 45 to 55%, and then spray dried. The spray dryer can be a pressure type, double stream type or centrifugal rotating disc type dryer. The centrifugal rotating disc type spray dryer is preferred, as it guarantees a good particle size distribution for the catalyst.

Calcination of the catalyst is done in two stages: decomposition of the salts of each element in the catalyst; and calcination at a high temperature. For decomposition, the temperature should be between 200 and 300° C and the time 0.5 to 2 hours. The calcination temperature is between 500 and 800° C, preferably between 550 and 700° C, and the time from 20 minutes to 2 hours. Decomposition and calcination can be performed separately, or in different parts of the same oven, or simultaneously in a rotating oven. A suitable amount of airflow air is needed in the oven during decomposition and calcination in order to prevent reduction.

In the catalyst of the present invention, the specifications for the propylene, ammonia, and molecular oxygen required to prepare acrylonitrile are the same as those of other ammoxidation catalysts. Even though the low molecular weight and hydrocarbon content of the raw materials have no effect upon reaction, from an economic viewpoint the concentration of propylene should be higher than 85% by mole. Ammonia can be a fertilizer-grade liquid ammonia. Pure oxygen or oxygen-enriched air is preferred for reaction, though for reasons of economy and resource availability it is better to use air as a source of oxygen.

The mole ratio of ammonium to propylene feeding to the fluidized-bed reactor is from 0.8 to 1.5, and preferably from 1.0 to 1.3. The air to propylene mole ratio is from 8.0 to 10.5, and preferably from 9.0 to 9.8. Should higher air ratios be necessary for any reason, they may reach 11.0 without a significant effect on reaction. However, for safety reasons the volume content of oxygen in the gaseous reactant should not be higher than 7%, and preferably not higher than 4%.

When the catalyst of the present invention is used in a fluidized-bed reactor, the reaction temperature should be from 420 to 470° C, and preferably from 425 to 450° C. The catalyst is suitable for use in conditions of slightly lower than normal reaction temperatures, high pressure and high loads, and as such the reaction pressure can exceed 0.08 MPa (for example: from 0.08 to 0.15 MPa). Reaction pressure below 0.08 MPa will show no unfavorable effect, and acrylonitrile single pass yields may increase further.

The propylene load of the catalyst (WWH) is from 0.06 to 0.15/hr, and preferably from 0.07 to 0.10/hr. Should the load be too low it will not only waste catalyst, but will also increase production of carbon dioxide and selectivity will decrease. An overly large load is not practically useful; with a catalyst feed that is too small, the heat-transferring area of the cold water pipe within the catalyst will be smaller than the area needed to remove the reaction heat, making the reaction temperature impossible to control.

With the catalyst of the present invention, existing production technology can be used for product recovery and refining. The unreacted ammonia in the effluent from the fluidized-bed reactor is removed in a neutralization tower, and all the organic components are absorbed in water at low temperature. Extractive distillation is used for removing hydrogen cyanide and water from the absorbed liquid, making for an acrylonitrile product of high purity.

As the magnesium in the component is beneficial for high loads, lowered reaction temperatures and lowered air to propylene ratios, tungsten can enhance the performance of the catalyst under high reaction pressures. By removing elements that have a negative effect upon reaction performance under high pressure and high loads, and increasing the amount of magnesium used, as well as using magnesium, manganese and tungsten at the same time, the catalyst obtains a better result when under a slightly lower than normal reaction temperature of 425° C, a high reaction pressure (0.14 MPa), a high load (WWH 0.085/hr). The single pass yield rate for acrylonitrile reaches 80.1% as well.

The catalyst of this invention was tested for activity in a fluidized-bed reactor having an inner diameter of 38 mm. The amount of catalyst used was 400 g, the reaction temperature was 425° C, pressure was 0.14 MPa, mole ratio was propylene:ammonia:air = 1:1.2:9.5, and WWH was 0.085/hr.

The definitions for the propylene conversion rate, acrylonitrile selectivity and single pass yield rates are as follows:

Propylene conversion rate (%)

$(\text{reaction propylene mole number} \div \text{propylene load mole number}) \times 100$

Acrylonitrile selectivity (%)

$(\text{produced acrylonitrile mole number} \div \text{reaction propylene mole number}) \times 100$

Acrylonitrile single pass yield rate (%)

$(\text{produced acrylonitrile mole number} \div \text{propylene load mole number}) \times 100$

This invention is elaborated further by the following embodiments.

#### EMBODIMENT 1

Material A was prepared by dissolving a mixture of 2.05 g cesium nitrate, 3.88 g sodium nitrate and 1.75 g potassium nitrate in 30 g of water by heating;

Material B was prepared by dissolving 12.5 g chromium trioxide in 15.0 g of water.

Material C was prepared by dissolving 21.68 g ammonium tungstate and 435.7 g ammonium molybdate in 350 g water of a temperature ranging from 60°C to 90°C;

Material D was prepared by dissolving a mixture of 65.0 g bismuth nitrate, 15.25 g of manganese nitrate, 290.5 g of nickel nitrate, 46.8 g of cerium nitrate, 98.5 g of magnesium nitrate and 175.25 g of iron nitrate in 250 g of water by heating;

Material E was a solution of 4.35 g of phosphoric acid.

Material A was mixed with 1280 g of 40% by weight silica sol, to which materials C, B, D and E were added while stirring. After thoroughly stirring, a slurry was formed, which was spray-dried according to conventional methods to obtain microspheres, followed by calcining at 600°C for 2 hours in a rotating oven with an inner-diameter of 89 mm and a length of 1700 mm (phi.89.times.1700 mm). The prepared catalyst had a composition as follows:

50%K<sub>0.1</sub>Na<sub>0.20</sub>Cs<sub>0.065</sub>P<sub>0.025</sub>Cr<sub>0.35</sub>Ce<sub>0.35</sub>Ni<sub>6.0</sub>Mg<sub>1.25</sub>Mn<sub>0.15</sub>W<sub>0.25</sub>Fe<sub>2.0</sub>Bi<sub>0.75</sub>Mo<sub>13.0</sub>O<sub>x</sub> + 50% SiO<sub>2</sub>.

#### EMBODIMENTS 2 to 8 and COMPARATIVE EXAMPLES 1 to 4

The catalysts below, with their different components, were prepared fundamentally by the process as described in Embodiment 1, and acrylonitrile was produced by a propylene ammoxidation reaction under the following reactive conditions with said catalysts. Please see results at Table 1.

The reactive conditions for the embodiments and comparative examples were as follows:

phi 38 mm fluidized-bed reactor



March 7, 2000 (00.03.07)

temperature: 425 °C

pressure: 0.14 MPa

catalyst load: 400 g

WWH: 0.085/hr

material ratio (mole):  $C_3 / NH_3 / air = 1/1.2/9.5$

Table 1

EMBODIMENT	CATALYST COMPOSITION	ACRYLONITRILE YIELD RATE%	ACRYLONITRILE SELECTIVITY %	PROPYLENE CONVERSION RATE %
Embodiment 1	$K_{0.1}Na_{0.20}Cs_{0.065}P_{0.025}Cr_{0.35}Ce_{0.33}Ni_{6.0}Mg_{1.23}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	80.1	81.9	97.8
Embodiment 2	$K_{0.1}Na_{0.20}Cs_{0.065}B_{0.02}Cr_{0.3}Ce_{0.33}Ni_{6.0}Mg_{1.23}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.3	81.4	97.4
Embodiment 3	$K_{0.1}Rb_{0.20}Cs_{0.05}B_{0.02}Cr_{0.3}La_{0.25}Ni_{6.0}Mg_{1.23}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.1	81.0	97.6
Embodiment 4	$Li_{0.1}Na_{0.20}Cs_{0.065}P_{0.025}Cr_{0.35}Ce_{0.4}Co_{2.5}Ni_{3.0}Mg_{1.25}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.5	81.3	97.8
Embodiment 5	$K_{0.15}Na_{0.20}Rb_{0.05}P_{0.025}Cr_{0.35}Ce_{0.33}Ni_{5.5}Mg_{1.23}Mn_{0.2}W_{0.35}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.8	81.4	98.0
Embodiment 6	$K_{0.15}Cs_{0.065}P_{0.025}Cr_{0.35}V_{0.1}Ni_{6.0}Cu_{0.15}Mg_{1.23}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.65}Mo_{13.0}O_x$	80.0	81.8	97.8
Embodiment 7	$K_{0.15}Rb_{0.065}P_{0.015}V_{0.1}Ni_{5.5}Cu_{0.15}Mg_{1.23}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.65}Mo_{13.0}O_x$	79.0	80.5	98.1
Embodiment 8	$Na_{0.1}Rb_{0.1}Cs_{0.025}B_{0.025}Cr_{0.3}La_{0.25}Co_{4.5}Sr_{0.33}Mg_{1.0}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.1	81.4	97.2
Comparative Example 1	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.0}Co_{5.0}Na_{0.15}Mn_{0.45}Cr_{0.45}K_{0.17}Cs_{0.05}O_x$	76.8		
Comparative Example 2	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.4}Co_{4.3}Na_{0.15}W_{0.45}Cr_{0.45}K_{0.15}Cs_{0.07}O_x$	77.1		
Comparative Example 3	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.0}Co_{5.0}Na_{0.15}Mn_{0.45}Cr_{0.45}K_{0.21}O_x$	76.2		
Comparative Example 4	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{5.0}Mg_{2.0}Na_{0.15}W_{0.45}Cr_{0.45}Cs_{0.09}O_x$	77.4		

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[54] 发明名称 丙烯氨氧化制丙烯腈的流化床催化剂

[57] 摘要

本发明涉及一种丙烯氨氧化制丙烯腈的流化床催化剂,含有二氧化硅载体和以原子比 计化学式如下的组合物:  $A_xB_yC_zMg_uMn_vW_tFe_sBi_rMo_iO_2$  式中 A 选自 Li、Na、K、Rb 或 Cs 中至少二种; B 选自 Co、Ni、Cr、Ca、Ce、La、Cu 或 V 中至少一种; C 选自 B、P 或 As 中至少一种。本发明催化剂特别适用于在较通常反应温度略低、低空气/丙烯比、较高的反应压力和高丙烯负荷条件下使用,且可保持很高的丙烯腈单收,可用于工业生产中。

## 权 利 要 求 书

- 1、一种丙烯氨氧化制丙烯腈的流化床催化剂，含有二氧化硅载体和以原子比计化学式如下的

组合物：



式中 A 选自 Li、Na、K、Rb 或 Cs 中至少二种；

B 选自 Co、Ni、Cr、Ca、Ce、La、Cu 或 V 中至少一种；

C 选自 B、P 或 As 中至少一种；

a 的取值范围为 0.01~1.5；

b 的取值范围为 0.1~10.0；

c 的取值范围为 0~0.6；

d 的取值范围为 0.8~7.5；

e 的取值范围为 0.01~2.5；

f 的取值范围为 0.05~1.5；

g 的取值范围为 0.1~4.0；

h 的取值范围为 0.2~2.5；

i 的取值范围为 12.0~14.5；

x 为满足催化剂中各元素化合价所需的氧原子总数；

其中催化剂载体选自二氧化硅，其用量以重量百分比计为 30~70%。

- 2、根据权利要求 1 所述丙烯氨氧化制丙烯腈的流化床催化剂，其特征在于 a 的取值范围为 0.01~0.7。

- 3、根据权利要求 1 所述丙烯氨氧化制丙烯腈的流化床催化剂，其特征在于 c 的取值范围为 0.01~0.45。

- 4、根据权利要求 1 所述丙烯氨氧化制丙烯腈的流化床催化剂，其特征在于 d 的取值范围为 1.0~4.0。

- 5、根据权利要求 1 所述丙烯氨氧化制丙烯腈的流化床催化剂，其特征在于 e 的取值范围为 0.2~1.5。

- 6、根据权利要求 1 所述丙烯氨氧化制丙烯腈的流化床催化剂，其特征在于 f 的取值范围为 0.1~1.0。

## 丙烯氨氧化制丙烯腈的流化床催化剂

本发明涉及一种丙烯氨氧化制丙烯腈的流化床催化剂。

丙烯腈是重要的有机化工原料，它是通过丙烯氨氧化反应生产的。为获得高活性、高选择性的流化床催化剂，人们经过不断探索，进行了一系列改进。这些改进大都涉及催化剂活性组成，注重催化剂活性组份之间的搭配，来提高催化剂的活性与选择性，从而达到丙烯腈单程收率的提高，以及生产负荷的提高。

氨氧化法生产丙烯腈经过 30 多年的发展，工厂的生产能力与市场需求已接近平衡。目前丙烯腈生产的主要发展趋势，已由注重建设新装置转向原有工厂的技术改造，以进一步降低原料消耗和增加生产能力。通过对原有工厂的改造，更换高效催化剂和消除生产工艺中的瓶颈，丙烯腈的生产能力有可能提高 50~80%，而所需的投资仅为新建装置的 20~30%，经济效益十分巨大。

工厂改造中会产生两个问题：①流化床反应器的反应压力将上升；②催化剂的装载量不能太多。为此要求换用的催化剂应有较高的丙烯负荷和能承受较高的反应压力。

流化床反应器的反应压力是由反应器出口到吸收塔顶之间一系列换热器、塔器和配管的阻力降决定的。由于生产能力的增加使反应器出口的物料量明显增大，使上述阻力降增加。另外，各换热器传热面积不够也需增加换热设备，使阻力降进一步增大。由于环保要求，吸收塔顶的反应废气不准直接排放到大气中，要送到炉子烧掉。这样如果不用引风机，则必须提高吸收塔顶压力。由于上述种种原因，目前反应器的操作压力比设计值要增加 0.5~1.0 倍，即达到 0.08MPa 以上。

上述第二个问题是催化剂的负荷，即 WWH。其定义是每吨催化剂，每小时可以处理丙烯的吨数。由于反应器进料量的增加，如果催化剂的负荷不变，则催化剂装载量也要相应增加。但原设计的流化床反应器中冷却水管高度不够，因此反应器中催化剂的流化高度有可能超过冷却水管的高度。另外，由于反应器进料量增大，所以操作线速也显著提高。这两项变化的综合影响有可能使反应器稀相温度上升，造成二氧化碳生成量增大，丙烯腈选择性下降。因此催化剂的 WWH 较高可以防止出现上述问题。

从理论上来说提高催化剂的 WWH 应当增加催化剂对丙烯的吸附活化能力，但目前尚

无催化剂中某种元素可以提高对丙烯吸附活化能力的报导。在文献 CN1021638C 中提出了如下组成的催化剂：



其中 A 为钾、铷、铯、钐、铈；B 为锰、镁、锆、钙、钡、镧、稀土元素；C 为磷、砷、硼、锑、铬；M 为钨、钼。

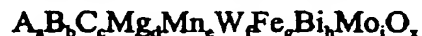
上述催化剂可以得到较高的丙烯腈单收，但催化剂的丙烯负荷较低，在较高的反应压力下丙烯腈单收下降较大。进一步研究表明，上述催化剂中的组分 B 和 M 对催化剂的负荷和在高压下的性能有关。组分 B 中的某些元素虽然对提高丙烯腈单收有作用，但对催化剂负荷的提高和高反应压力的性能有负面影响，不利于催化剂适应较高压力，较高负荷条件下操作。另外在 CN1021638C 中曾规定上述催化剂组成中，i 和 j 的总和为 12，即是一个常数。在本发明中取消此项规定，因为按此规定 M 组分增加时钼组分将减少，将影响丙烯腈单收。

文献 US5093299 和 US5212137 中介绍了一种使用钼、铋、铁、镍、镁、钾和铯体系的催化剂进行丙烯氨氧化制备丙烯腈的催化剂。从其实施例中看出，其催化体系是不含钠的，任选元素中虽提到稀土金属元素铈和铬，但是仅作为任选元素使用。实施例中并没有公开其它稀土元素与铬和镁元素的搭配使用情况。实施例的考察条件为固定床，430℃ 反应温度，没有提及实验操作中具体的反应压力与操作负荷情况数据。该固定床考察条件难以反映流化床操作的真实情况。该专利中介绍，其催化剂能在通常略低的反应温度下操作，其具有较高的催化活性及优良的氧化还原稳定性，因而可适用于较低的空气/丙烯比条件操作。

文献平 8-27089 中介绍了一种丙烯腈的制造方法。其采用钼、铋、铁、镁和钨体系的催化剂进行丙烯氨氧化反应，该文献实施例中的考察条件为常压，没有提及在高压、高操作负荷条件下的情况数据。

本发明的目的是要克服上述文献中存在的催化剂未涉及较高反应压力和操作负荷的问题，提供一种新的生产丙烯腈的流化床催化剂。该催化剂能适应在较通常略低的反应温度、较高的反应压力和较高的负荷条件下操作，且保持高的丙烯腈单程收率。

本发明的目的是通过以下的技术方案来实现的：一种生产丙烯腈的流化床催化剂，含有二氧化硅载体和以原子比计化学式如下的组合物：



式中 A 选自 Li、Na、K、Rb 或 Cs 中至少二种；

B 选自 Co、Ni、Cr、Ca、Ce、La、Cu 或 V 中至少一种；

C 选自 B、P 或 As 中至少一种；

a 的取值范围为 0.01~1.5；

b 的取值范围为 0.1~10.0；

c 的取值范围为 0~0.6；

d 的取值范围为 0.8~7.5；

e 的取值范围为 0.01~2.5；

f 的取值范围为 0.05~1.5；

g 的取值范围为 0.1~4.0；

h 的取值范围为 0.2~2.5；

i 的取值范围为 12.0~14.5；

x 为满足催化剂中各元素化合价所需的氧原子总数；

其中催化剂载体选自二氧化硅；其用量以重量百分比计为 30~70%。

上述技术方案中 a 的取值优选范围为 0.01~0.7，c 的取值优选范围为 0.01~0.45，d 的取值优选范围为 1.0~4.0，e 的取值优选范围为 0.2~1.5，f 的取值优选范围为 0.1~1.0。

本发明催化剂的制造方法并无特殊要求，可按常法进行。首先将催化剂各组份制成溶液，再与载体混合制成浆料，经喷雾干燥成型为微球状，最后焙烧制成催化剂。浆料的配制最好按 CN1005248C 方法进行。

制造本发明催化剂的原料为：

催化剂中的钼组份用氧化钼或钼酸铵。

催化剂中的磷、砷和硼最好用相应的酸类或其铵盐；钨可用钨酸铵或氧化钨；铬最好用三氧化铬、硝酸铬或二者的混合物；其余组分最好用其硝酸盐、氢氧化物或可分解为氧化物的盐类。

作为载体二氧化硅的原料可用硅溶胶、硅凝胶或两者的混合物。如果用硅溶胶，其质量要符合 CN1005248C 的要求。

配制好的浆料加热浓缩到固含量为 47~55%后喷雾干燥。喷雾干燥器可用压力式，两流式或离心转盘式，但以离心式较好，能保证制成的催化剂有良好的粒度分布。

催化剂的焙烧可分为两个阶段进行：催化剂中各元素盐类的分解和高温焙烧。分解阶段温度最好为 200~300℃，时间为 0.5~2 小时。焙烧温度为 500~800℃，最好为 550~700℃；焙烧时间为 20 分钟到 2 小时。上述分解和焙烧在两个焙烧炉内分别进行，也可在

一个炉内分为两个区域，也可在连续式旋转焙烧炉内同时完成分解和焙烧。在催化剂分解和焙烧过程中要通入适量空气，防止催化剂被过度还原。

采用本发明催化剂制造丙烯腈所需的丙烯、氨和分子氧的规格与使用其它氨氧化催化剂相同。虽然原料丙烯中的低分子饱和烃含量对反应并无影响，但从经济观点考虑丙烯浓度最好大于 85%(摩尔)。氨可用肥料级液氨。反应所需分子氧从技术角度可用纯氧，富氧和空气，但从经济和安全考虑最好用空气。

进入流化床反应器的氨与丙烯的摩尔比为 0.8~1.5 之间，最好为 1.0~1.3。空气与丙烯的摩尔比为 8~10.5，最好为 9.0~9.8。如果由于某些操作上的原因须用较高空气比时，可以增大到 11，对反应没有重大影响。但从安全考虑，反应气体中的过量氧不能大于 7%(体积)，最好不大于 4%。

本发明催化剂用于流化床反应器时，反应温度为 420~470℃，最好为 425~450℃。本发明催化剂是一种适用于较通常略低的反应温度，高压、高负荷催化剂，因此在生产装置中反应压力可在 0.08MPa 以上，例如，0.08~0.15MPa。如果反应压力低于 0.08MPa 也不会有任何不利影响，丙烯腈单收可进一步提高。

本发明催化剂的丙烯负荷(WWH)为 0.06~0.15 小时<sup>-1</sup>，最好为 0.07~0.10 小时<sup>-1</sup>。负荷过低不仅浪费催化剂，也会使二氧化碳生成量增加，选择性下降，是不利的。负荷过高没有实际意义，因为催化剂加入量过少，会使催化剂层内冷却水管的传热面积小于移去反应热所需的面积，造成反应温度无法控制。

用本发明催化剂制造丙烯腈的产品回收精制工艺，可用已有的生产工艺，不需做任何改造。即流化床反应器的流出气体经中和塔除去未反应氨，再用低温水将全部有机产物吸收。吸收液经萃取蒸馏，脱氢氰酸和脱水处理后得高纯度丙烯腈产品。

由于组分中的镁对提高负荷、降低反应温度及降低空气/丙烯比有利，钨可以改进催化剂在高反应压力下的性能，因此去掉一些对高压、高负荷反应性能有负面影响的组分，增加镁的使用量，以及镁、锰和钨同时使用，使催化剂具有了在较通常略低的反应温度 425℃、较高反应压力(0.14MPa)、较高负荷(WWH 为 0.085 小时<sup>-1</sup>)条件下的操作能力，且丙烯腈单程收率最高达到了 80.1%的水平，取得了较好的效果。

本发明催化剂的活性考评是在内径为 38 毫米的流化床反应器中进行的。催化剂装填量 400 克，反应温度 425℃，反应压力 0.14MPa，原料配比(摩尔)为丙烯：氨：空气=1：1.2：9.5，催化剂的丙烯负荷(WWH)为 0.085 小时<sup>-1</sup>。

在本发明中丙烯转化率、丙烯腈选择性和单程收率的定义如下：



$$\text{丙烯转化率 (\%)} = \frac{\text{反应的丙烯摩尔数}}{\text{丙烯进料摩尔数}} \times 100$$

$$\text{丙烯腈选择性 (\%)} = \frac{\text{生成丙烯腈摩尔数}}{\text{反应的丙烯摩尔数}} \times 100$$

$$\text{丙烯腈单程收率 (\%)} = \frac{\text{生成丙烯腈摩尔数}}{\text{丙烯进料摩尔数}} \times 100$$

下面通过实施例对本发明作进一步的阐述。

### 【实施例 1】

将 2.05 克硝酸铯、3.88 克硝酸钠与 1.75 克硝酸钾混合，加水 30 克并加热后溶解，得到物料(A)；将 12.5 克三氧化铬溶于 15 克水中，得物料(B)；将 21.68 克钨酸铵以及 435.7 克钼酸铵溶于 350 克 60~90℃热水中，得物料(C)；将 65.0 克硝酸铋、15.25 克硝酸锰、290.5 克硝酸镍、46.8 克硝酸铈、98.5 克硝酸镁和 175.25 克硝酸铁混合，加水 250 克，加热溶解后作为物料(D)；称取磷酸溶液 4.35 克作为物料(E)。

将物料(A)与 1280 克重量浓度为 40%的硅溶胶混合，在搅拌下依次加入物料(C)、(B)、(D)和(E)，经充分搅拌后得浆料，依常法将制成的浆料在喷雾干燥器中进行微球粒成型，最后在内径为 89 毫米，长度为 1700 毫米( $\phi 89 \times 1700$  毫米)的旋转焙烧炉中于 600℃焙烧 2.0 小时，制成组成为



### 【实施例 2~8 及比较例 1~4】

采用与实施例 1 基本相同的方法制备具有下表中不同组成的催化剂，并用所制得的催化剂在下述的反应条件下进行丙烯氨氧化生成丙烯腈的反应，结果见表 1。

上述实施例与比较例的反应条件为：

$\phi 38$  毫米流化床反应器

反应温度 425℃

反应压力 0.14MPa

催化剂装填量 400 克

催化剂丙烯负荷(WWH) 0.085 小时<sup>-1</sup>

原料配比(摩尔)  $\text{C}_3\text{H}_6/\text{NH}_3/\text{空气} = 1/1.2/9.5$

表 1

实施例	催 化 剂 组 成	丙烯腈收率%	丙烯腈选择性%	丙烯转化率%
实施例 1	$K_{0.1}Na_{0.20}Cs_{0.065}P_{0.0025}Cr_{0.35}Ce_{0.35}Ni_{6.0}Mg_{1.25}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	80.1	81.9	97.8
实施例 2	$K_{0.1}Na_{0.20}Cs_{0.065}B_{0.02}Cr_{0.30}Ce_{0.35}Ni_{6.0}Mg_{1.25}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.3	81.4	97.4
实施例 3	$K_{0.10}Rb_{0.20}Cs_{0.05}B_{0.02}Cr_{0.30}La_{0.25}Ni_{6.0}Mg_{1.25}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.1	81.0	97.6
实施例 4	$Li_{0.1}Na_{0.20}Cs_{0.065}P_{0.0025}Cr_{0.35}Ce_{0.40}Co_{2.5}Ni_{3.0}Mg_{1.25}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.5	81.3	97.8
实施例 5	$K_{0.15}Na_{0.20}Rb_{0.05}P_{0.0025}Cr_{0.35}Ce_{0.35}Ni_{5.5}Mg_{1.25}Mn_{0.20}W_{0.35}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.8	81.4	98.0
实施例 6	$K_{0.15}Cs_{0.065}P_{0.0025}Cr_{0.35}V_{0.1}Ni_{6.0}Cu_{0.15}Mg_{1.2}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.65}Mo_{13.0}O_x$	80.0	81.8	97.8
实施例 7	$K_{0.15}Rb_{0.065}P_{0.015}V_{0.1}Ni_{5.5}Cu_{0.15}Mg_{1.25}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.65}Mo_{13.0}O_x$	79.0	80.5	98.1
实施例 8	$Na_{0.1}Rb_{0.1}Cs_{0.025}B_{0.025}Cr_{0.30}La_{0.25}Co_{4.5}Sr_{0.35}Mg_{1.0}Mn_{0.15}W_{0.25}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.1	81.4	97.2
比较例 1	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.0}Co_{5.0}Na_{0.15}Mn_{0.45}Cr_{0.45}K_{0.17}Cs_{0.05}O_x$	76.8		
比较例 2	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.4}Co_{4.3}Na_{0.15}W_{0.45}Cr_{0.45}K_{0.15}Cs_{0.07}O_x$	77.1		
比较例 3	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.0}Co_{5.0}Na_{0.15}Mn_{0.45}Cr_{0.45}K_{0.21}O_x$	76.2		
比较例 4	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{5.0}Mg_{2.0}Na_{0.15}W_{0.45}Cr_{0.45}Cs_{0.09}O_x$	77.4		